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REVIEW

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Crystal engineering of porous coordination networks for C3 hydrocarbon separation

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Abstract

C3 hydrocarbons (HCs), especially propylene and propane, are high-volume products of the chemical industry as they are utilized for the production of fuels, polymers, and chemical commodities. Demand for C3 HCs as chemical building blocks is increasing but obtaining them in sufficient purity (>99.95%) for polymer and chemical processes requires economically and energetically costly methods such as cryogenic distillation. Adsorptive separations using porous coordination networks (PCNs) could offer an energy-efficient alternative to current technologies for C3 HC purification because of the lower energy footprint of sorbent separations for recycling versus alternatives such as distillation, solvent extraction, and chemical transformation. In this review, we address how the structural modularity of porous PCNs makes them amenable to crystal engineering that in turn enables control over pore size, shape, and chemistry. We detail how control over pore structure has enabled PCN sorbents to offer benchmark performance for C3 separations thanks to several distinct mechanisms, each of which is highlighted. We also discuss the major challenges and opportunities that remain to be addressed before the commercial development of PCNs as advanced sorbents for C3 separation becomes viable.

KEYWORDS
binding sites, C3 hydrocarbon, PCNs, separation

1 | INTRODUCTION

The energy footprint of the chemical industry is as high as 50% of industrial energy use and the separation or purification of products and feedstocks accounts for about 15% of global energy use across sectors.[1] A majority of these separations are driven by heat-induced processes and could be made up to 10 times more efficient by the introduction of nonthermal alternatives.[2] With the recent transition of the chemical industry to a dependence on gaseous feedstocks, aptly called the "Age of Gas,"[3] the development of new and more energy-efficient gas separation technologies is key to reducing the energy footprint of chemical commodity production, which continues to rise. The largest volume building blocks in the chemical industry are the light olefins, namely ethylene and propylene. Worldwide production of propylene reached 120 million tons in 2017, second only to ethylene.[4] Although ethylene is the number one chemical

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feedstock by volume, propylene occupies a vital position in the production of chemical industry products as it is a precursor for a wide range of commercially important higher-value chemicals.

Industrial methods of C3 HC production and their utility as feedstocks are detailed in Figure 1. Propylene is primarily produced from steam cracking of paraffins from natural gas or petroleum gas.[5] Steam cracking is an energy-intensive process that accounts for 20% of the chemical industry's energy use.[6] Purified propane, extracted by cryogenic distillation from paraffin mixtures, is used as a chemical feedstock. Indeed, propylene can be produced from the cracking of pure propane. Propane is also widely used as a fuel, being the primary component of liquefied petroleum gas. The presence of an unsaturated C═C double bond in propylene tends to result in incomplete combustion. Commercial fuel-grade propane is therefore typically purified to <5% propylene (HD-5 specifications).[7] Propyne and propadiene are by-products of the steam cracking process and can comprise up to 6% of the crude C3 fraction. Unfortunately, these C3 HCs can interfere with industrial processes that use propylene as a feedstock. Chemical grade propylene is typically required to have an MAPD (methylacetylene and propadiene) content of <20 ppm, and polymer grade propylene is required to have <2 ppm (or <1 ppm) MAPD, with an overall purity of >99.95%. Propyne has use as a chemical feedstock in acrylate production, and MAPD mixtures were briefly used as an acetylene substitute in welding. However, the MAPD fraction is normally catalytically hydrogenated to propane/propylene in the cracking process.[8] Nearly two-thirds of the global supply of propylene is utilized to produce polypropylene, which is in turn used for the production of commercial commodities including films, fibers, containers, packaging, caps, and closures. A number of other chemical products, such as phenol, propylene glycol, isopropanol, and acetone are produced from pathways that use propylene as a key feedstock.

The key message from this summary of the production and uses of C3 HCs is that separation of propylene from propane, propane from propylene, MAPD from propylene, and propane from other paraffins are key to a number of industrial processes and account for a major share of their energy footprints. The dominant technology for propane purification from gas streams and for propane/propylene separation is cryogenic distillation. Temperatures below 200 K, pressures of up to 28 atm, >100 distillation trays, and reflux ratios as high as 20 are needed to meet polymer grade specifications.[9,10]

It is, therefore, unsurprising that the development of new energy-efficient and environmentally friendly separation approaches for the purification of C3 HCs has been attracting attention in the academic and industrial communities. Indeed, C3 purification was recently highlighted as "one of the seven purifications that can

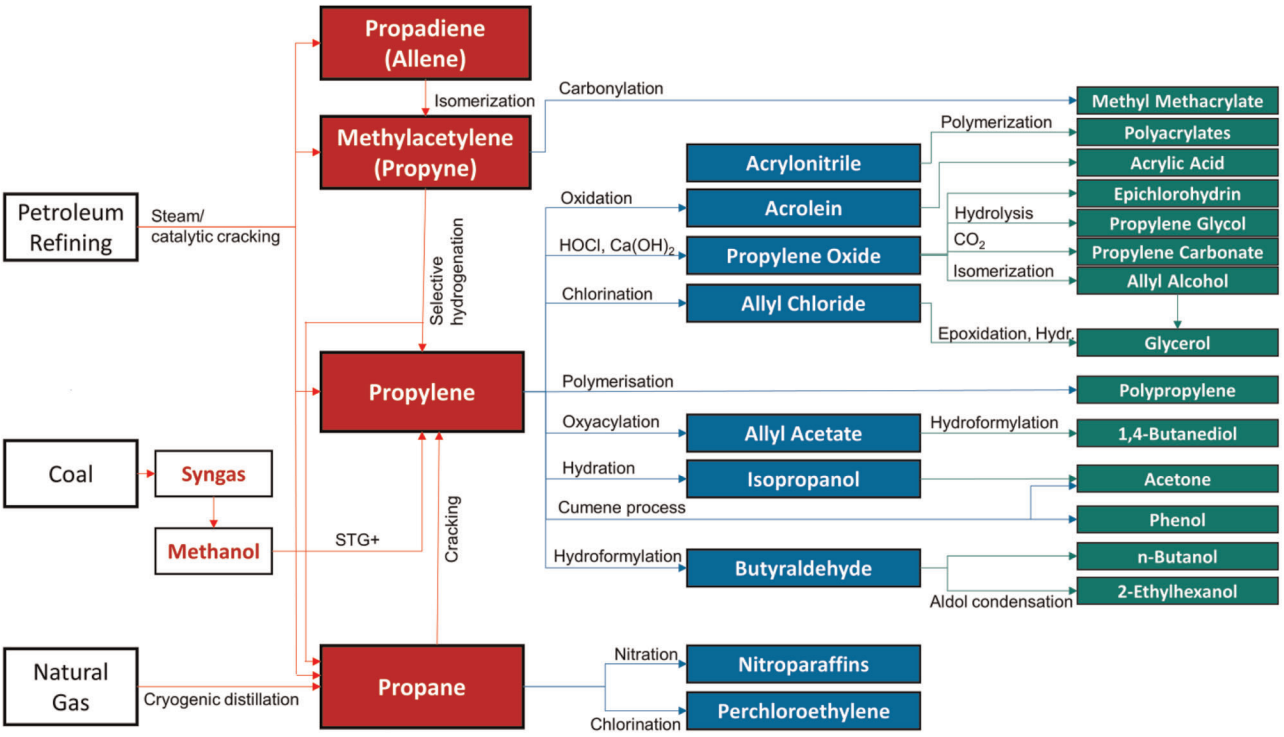
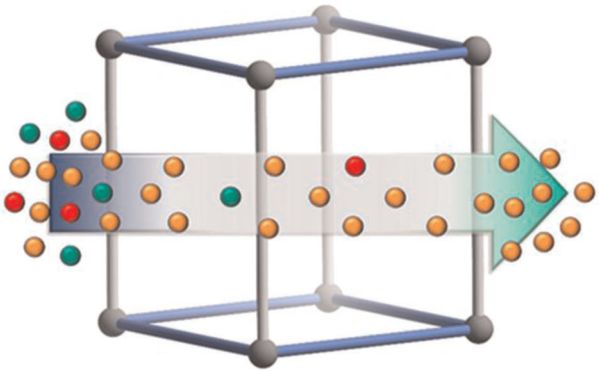


FIGURE 1 A schematic diagram that highlights industrial routes for the production of C3 HCs and products derived from C3 HCs. HC, hydrocarbon.

change the world."[1] Alternative approaches, such as gas-liquid absorption for the purification of propane from natural gas streams are less energy-intensive, but have lower efficiency and selectivity. Other processes, based on membranes or pi-complexation using Ag^+ or Cu^+ ions, are prone to deactivation by impurities and are operationally expensive. It is in this context that solid adsorbents are attractive as they typically offer facile recycling and low operating costs.

Adsorbent-based physisorption, therefore, offers an opportunity to replace the traditional energy-intensive processes that have remained largely unchanged for a century (e.g. distillation, solvent extraction, chemisorption) and fulfill the requirements for more energy-efficient purification processes.[11,12] Several classes of adsorbents, such as zeolites and activated carbon, have been explored for C3 hydrocarbon (HC) separation.[13–16] However, thus far, the separation performances of these materials are poor as it is difficult to fine-tune pore structure (size, shape, and chemistry) at the molecular level in such sorbents.[17,18] These separations are challenging for sorbents because of similarities in the physicochemical properties of C3 HCs (Figure 2). Porous coordination networks (PCNs),[23,24] which comprise metal-organic frameworks (MOFs), porous coordination polymers (PCPs),[25,26] and hybrid ultramicroporous materials (HUMs),[27–29] exploit the modularity of their building blocks (metal ions/clusters, organic/inorganic linkers) to control topology, pore size, and pore chemistry in a manner that is infeasible for existing classes of materials.[30,31] PCNs can be readily assembled using crystal engineering principles[32–36] including the node-and-linker,[37,38] molecular building block (MBB),[34–36,39] and supramolecular building block approaches.[40,41] Precise control over pore structure can be exerted by adjustment of the lengths, geometry, and functionality of the MBBs.[42] There are numerous PCNs in the literature that provide a library of tens of thousands of sorbent candidates for the investigation of adsorptive gas separation performance. Further, the availability of detailed structural information has enabled combined experimental (e.g., in situ PXRD) and molecular modeling methods to provide insight into the mechanisms of selective sorption.[43,44]

In this review, we start with a discussion on the unparalleled modularity of PCNs, with a particular focus on the pore systems, followed by an analysis of recent progress concerning C3 HC separation using PCNs. In carrying out this analysis, we present case studies of PCNs used to separate C3 HCs by addressing the multiple mechanisms of separation. In many cases, PCNs outperform commercial state-of-the-art adsorbents such as zeolites and activated carbon. However, other factors are relevant with respect to commercialization and we outline the major challenges and opportunities associated with C3 HC separations.



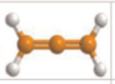
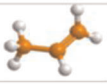
				
Adsorbate molecules	C_3H_4 (MA)	C_3H_4 (PD)	C_3H_6	C_3H_8
Boiling point (K)	250	239	225	231.
Dipole moment ($x10^{18}$ / e.s.u. cm)	0.75	0	0.366	0.084
Polarizability ($x10^{-25}$ cm^3)	55.5	56.9	62.6	62.9-63.7
Kinetic diameter (Å)	4.2	-	4.7	4.3-5.1

FIGURE 2 Schematic representation of C3 HC separation using PCNs.[19–22] (C_3H_4, propyne/methylacetylene; C_3H_4 (PD), propadiene/allene). HC, hydrocarbon; PCN, porous coordination network

2 | CRYSTAL ENGINEERING OF PCNS

Compared with traditional adsorbents, the modularity of PCNs enables crystal engineering of structure to design pore structure from first principles and to conduct systematic experiments that offer insight into structure-function relationships.[45,46] Whereas the focus herein is the importance of pore structure with respect to gas separations, this ability to control pore structure means that PCNs have also attracted considerable interest for other applications, especially gas storage,[47] catalysis,[48] and sensing.[49]

Pore size and shape control: Precise control over pore size and shape is crucial for the design of sorbents for C3 HC separations, especially for molecular sieving and the most challenging gas separations where the physicochemical properties of sorbates are similar.[50] The main approaches adopted to precisely control pore size are through ligand substitution or postsynthetic modification.[51]

The development of families or platforms illustrates the power of isoreticular approaches to the design of porous sorbents.[52] Judicious selection of metal nodes, organic linkers, and inorganic pillars is exemplified by SIFSIX networks, which enable fine-tuning of pore structure to generate a platform of SIFSIX network variants that offer benchmark performance for address challenging gas separations (Figure 3).[53–57] Other strategies established for pore size control in PCNs include interpenetration,[58–60] pore space partition through in situ or postsynthetic insertion of size-matched molecular partitions onto the framework,[61–63] postsynthetic modification,[64] and conformational switching of some light-responsive organic moieties such as azobenzene.[65–68] It is notable that interpenetration, a phenomenon historically seen as a hindrance due to the inevitable reduction in surface area, can be used to reduce pore size and increase hydrolytic stability.[69] With respect to SIFSIX networks, interpenetration has been shown to be a useful strategy to systematically control the pore aperture, with pore size reduction greatly improving selectivity, and to improve hydrolytic stability to the point that water sorption processes can be reversible.[53]

Pore chemistry (functional group) control: In addition to pore size and shape, the incorporation of specific functionality into the internal surface of PCNs enables selective recognition of molecules through strong binding interactions including H-bonding,[70,71] coordination chemistry,[72–76] and covalent bond formation.[77] Interactions involving coordinatively unsaturated metal sites (UMCs) have been widely investigated thanks to there being numerous PCN platforms with UMCs. With respect to C3 HCs, selective recognition of propylene can occur through interaction between a UMC and the π-electrons of the olefinic bond.[78] Such binding sites can be incorporated through the use of linkers with appropriate functionality. For example, the utilization of metalloligands is a convenient method to introduce UMCs.[79–81] Another established approach is to functionalize pore surface via postsynthetic modification.[82,83] Pore size and pore surface can both be controlled via postsynthetic modification, for example, functionalization of either UMC nodes or organic linkers.[77,84] In the case of charged frameworks, counterions residing in voids can be exchanged with other ionic species of different size and chemistry.[85,86]

3 | CHRONOLOGY OF THE DEVELOPMENT OF PCNS FOR C3 HC SEPARATION

3.1 | C_3H_6/C_3H_8 separation

Interest in the potential utility of PCNs for C3 HC separations is a relatively recent phenomenon (Figure 4).[98,99] Compared with C_2H_4/C_2H_6 separation, materials that display selectivity for C_3H_6/C_3H_8 are relatively understudied.[100–103] The first reported study of C_3H_6/C_3H_8 separation by a PCN was conducted upon the MOF Cu-BTC (also known as HKUST-1, benzene-1,3,5-tricarboxylate [BTC]) by Lamia et al.[87] in 2009. Strong C_3H_6/C_3H_8 separation performance was attributed to the vacant s-orbital of the unsaturated Cu(II) cations bonding with the π-orbital of propylene. In the same year, Li et al.[88] demonstrated the first examples of kinetic separation of C_3H_6 and C_3H_8 by exploiting the markedly different diffusion rates of C3 HC mixtures. Specifically, the authors demonstrated that materials such as Zn $(2\text{-cim})_2$ and $Zn(2\text{-bim})_2$ (2-chloroimidazole [2-cim], 2-bromoimidazole [2-bim]) have essentially identical uptake capacities for C_3H_6 and C_3H_8 under equilibrium conditions, but display markedly faster adsorption kinetics for C_3H_6 than C_3H_8. In 2012, Bae et al.[104] reported C_3H_6 over C_3H_8 selectivity in three M-MOF-74 materials (M = Co, Mn, and Mg) possessing high densities of UMCs. Among them, the C_3H_6/C_3H_8 selectivity of Co-MOF-74 had the highest value of ca. 46. Similarly, in 2017, Long's

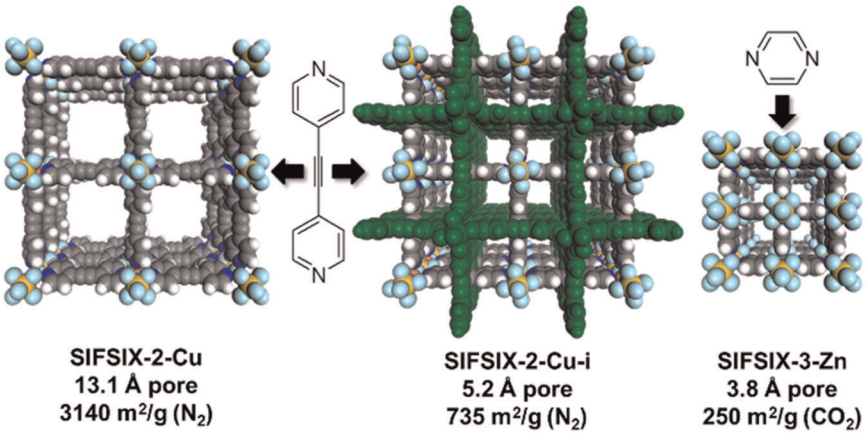


FIGURE 3 Pore size control via linker length variation and interpenetration as illustrated in the SIFSIX platform (reprinted with permission from Ref. 53. Copyright 2013, Springer Nature)

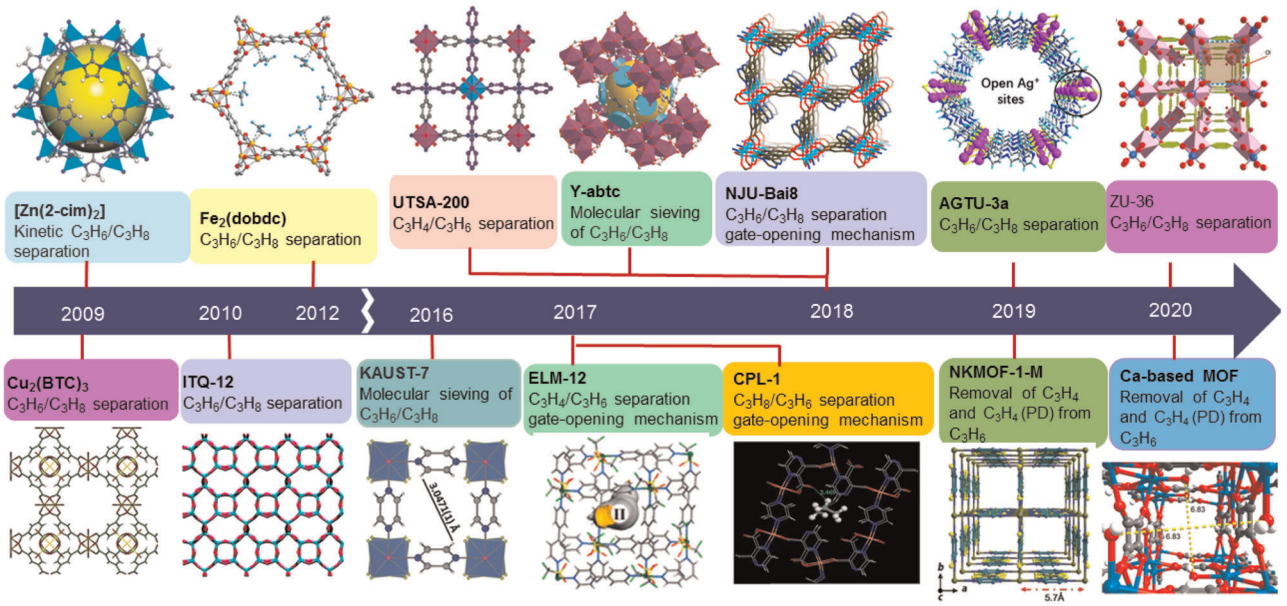


FIGURE 4 Chronology of key developments with respect to the use of PCNs for C3 hydrocarbon separation (reprinted with permission from Refs. 4,71,78,87–97. Copyright 2009, American Chemical Society; Copyright 2009, Elsevier B.V.; Copyright 2010, American Chemical Society; Copyright 2012, American Association for the Advancement of Science; Copyright 2016, American Association for the Advancement of Science; Copyright 2016, American Chemical Society; Copyright 2017, Elsevier B.V.; Copyright 2018, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim; Copyright 2018, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim; Copyright 2018, Elsevier B.V.; Copyright 2019, The Royal Society of Chemistry; copyright 2019, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim; Copyright 2020, American Chemical Society; Copyright 2020, American Chemical Society). PCN, porous coordination network

group evaluated a series of M_2(m-dobdc) (M = Mn, Fe, Co, Ni; 4,6-dioxido-1,3-benzenedicarboxylate [m-dobdc^{4-}]) for C_3H_6/C_3H_8 selectivity.[105] Compared with the isostructural M-MOF-74 materials, M_2(m-dobdc) exhibits stronger binding interactions with C3 HCs. Among these four materials, Fe_2(m-dobdc) was found to exhibit the highest C_3H_6/C_3H_8 (>55) selectivity. In 2016, Cadiau et al.[89] developed a fluorinated porous PCN(NbOFFIVE-1-Ni, also referred to as KAUST-7) for the size exclusion-based separation of C_3H_6/C_3H_8. Similarly, in 2020, Xing et al.[90] also demonstrated that two anion-pillared HUMs (GeFSIX-3-Ni and GeFSIX-3-Co, also denoted as ZU-36) exhibit efficient separation for C_3H_6/C_3H_8. Other examples of C_3H_6 from C_3H_8 separation include ITQ-12, CPL-1, Y-abc, NJU-Bai8, Zn_2(5-AIP)$_2$(BPY), MIL-100(Fe), AGTU-3a, MAF-23-O, Co(AIP)(BPY)$_{0.5}$, MCF-56/57, ZU-32, SIFSIX-2-Cu-i.[91–95,106–111]

All the aforementioned PCNs are selective for C_3H_6 over C_3H_8; reports of inverse selectivity, C_3H_8-selective materials, are rare.[112–115] In 2020, Yang et al.[113] reported that the ultramicroporous material, [Ni(bpe)$_2$(WO_4)] (1,2-bis(4-pyridyl) ethylene [bpe]), a HUM with mmo topology, is a C_3H_8-selective material. Indeed, it set a record for C_3H_8/C_3H_6 selectivity (1.62–2.75) and adsorption enthalpy (ca. 42 kJ/mol), attributed to multiple weak interactions. ZIF-7 and ZIF-8 are two other examples of C_3H_8-selective sorbents.[114,115]

3.2 | C_3H_4/C_3H_6 separation

C_3H_4/C_3H_6 separation is understudied with very few reports that address this separation.[116,117] In 2017, Li et al.[96] reported C_3H_4/C_3H_6 separation with the sql network [Cu(bpy)$_2$(OTf)$_2$] (ELM-12). ELM-12 was found to exhibit high selectivity for C_3H_4 over C_3H_6 (84 for a 1:99 mixture), which was attributed to cavities that are shaped to form a better fit with C_3H_4 than C_3H_6. Recently, a terbium PCN [Tb_2(TFBPDC)$_3$(H_2O)] (JXNU-6) with a novel fluorinated ligand was reported[118] to exhibit large C_3H_4 uptake and modest C_3H_4/C_3H_6 selectivity. The selectivity towards C_3H_4 was attributed to C—H···F hydrogen bonds between propyne molecules and the F atoms of the linker ligands. Other reports of selective adsorption of C_3H_4 over C_3H_6 have focused on hybrid porous materials with inorganic anionic pillars of SiF_6^{2-}, TiF_6^{2-}, and GeF_6^{2-}, exemplified by ZJUT-1, SIFSIX-14-Cu-i (UTSA-200), TIFSIX-14-Cu-i (ZU-13), and GeFSIX-dps-Cu/Zn.[58,119–121]

3.3 | C_3H_4/C_3H_4 (PD)/C_3H_6 (C_3H_4 propadiene/allene [PD])

The one-step separation of multicomponent C3 HC mixtures containing trace propyne, trace propadiene and propylene is

challenging but relevant since it represents industrial processes.[97,117] In 2018, Yang et al.[20] reported on the novel $NbOF_5^{2-}$ pillared HUM NbOFFIVE-2-Cu-i (ZU-62) with respect to its removal of trace propyne and trace propadiene from propylene. Whereas the parent HUM SIFSIX-2-Cu-i has uniform binding sites,[70] ZU-62 has three binding sites (Site I 6.75 Å, Site II 6.94 Å, Site III 7.20 Å). At the time, ZU-62 displayed a new record for C_3H_4 (PD) uptake (1.74 mmol/g), high C_3H_4 uptake (1.87 mmol/g), and very low uptake, 0.05 mmol/g, for C_3H_6 at 5000 ppm and 298 K. This was attributed to the presence of a C_3H_4-selective Site III and a C_3H_4 (PD)-selective Site I. Breakthrough tests for $C_3H_4/C_3H_4(PD)/C_3H_6$ (0.5:0.5:99) mixtures afforded an ultra-pure stream of C_3H_6 (over 99.9999%) through a one-step purification process. Subsequently, Peng et al.[4] reported two ultra-microporous PCNs, NKMOF-1-M (M = Cu, Ni), which exhibited benchmark selectivity for ternary $C_3H_4/C_3H_4(PD)/C_3H_6$ (0.5:0.5:99) mixtures. Recently, a Ca-based MOF studied by Li et al.[97] was also reported to simultaneously remove C_3H_4 and $C_3H_4(PD)$ from a ternary mixture of $C_3H_4/C_3H_4(PD)/C_3H_6$. This sorbent displayed record-high C_3H_4 and $C_3H_4(PD)$ uptake capacities (2.44 and 2.64 mmol/g, respectively) at 5 mbar attributed to multiple C—H···O binding interactions and π—π stacking. This Ca-based framework is the current benchmark for multicomponent C3 HC mixture separations at ambient conditions.

4 | MECHANISM OF C3 HC SEPARATIONS

As observed for other light HC separations in PCNs,[122–124] the separation of C3 HCs can be achieved via equilibrium (thermodynamic), nonequilibrium (kinetic, molecular sieving),[125] gate opening-based mechanisms, or combinations thereof.[116,126] For thermodynamically controlled separations, the difference in affinity between specific adsorbates and adsorbent surfaces results in binding sites that play a key role as other gaseous species also have access to the internal pore surface.[44,123] In other words, optimal binding sites immobilized onto pore surfaces, such as UMCs and hydrogen bonding donors/acceptors,[20,78,105] can enable preferential sorption of target components over others through host–guest interactions. For example, propylene selectivity over propane is often driven by interactions involving the π-electrons of the olefin double bond[106] whereas the recognition of propyne over propylene is frequently enabled by hydrogen bonding interactions involving the relatively acidic alkyne CH moiety of propyne.[70,71] If the diffusion rates of different components in the pore of PCNs vary as a result of, for example, subtle affinity differences or steric hindrance, kinetic separation can dominate.[107,127] Molecular-sieving-based separation is conceptually more straightforward as only targeted components can permeate the pore while others are inhibited. Sieving is promising for the development of high capacity and highly selective separations with negligible influence from coadsorption.[89,128] Given the small kinetic diameter difference between C3 HCs, the pore system of PCNs must be selected or designed very precisely if molecular sieving-based separation is the goal.[129] Additionally, the flexible and dynamic nature of some PCNs may be exploited for use in separation applications.[130–133] Gate-opening behavior in PCNs can result in structural transitions from a closed or "less-open" phase, to an open phase induced by gas sorption. Specific threshold pressures can thereby control the uptake and release of adsorbed guests.[30,134–138] The specific threshold pressure, or opening pressure, imparted by gas molecules also enables the application of PCNs in the recognition and separation of different components.[139–142]

4.1 | Thermodynamic equilibrium separation

Thermodynamic equilibrium separation of C3 analogs driven by selective binding sites is one of the most powerful and effective approaches for separations, especially when trace impurities are present and high purity is specified.[108,126] As discussed below, such processes may be driven by binding sites with functional groups that feature UMCs, π-complexing agents, hydrogen bonding interactions, van der Waals interactions, CH-π interactions or a combination thereof.[65,100,143]

UMC driven selective adsorption and separation: The π electrons of the double bond of propylene typically result in specific binding interactions with the vacant orbital of unsaturated metalsites.[9] For example, the MOF-74 platform of materials was systematically studied for C_3H_6/C_3H_8 selectivity by the Long group.[78] They demonstrated preferential adsorption of C_3H_6 over C_3H_8 which was attribute to relatively strong interactions between the high density of UMCs and C_3H_6 versus C_3H_8 (Figure 5A).

4.1.1 | Hydrogen bonding interactions

Hydrogen bonding can also be used to enable the removal of propyne from other C3 HCs thanks to the strong hydrogen bonding interactions that may be formed between acidic alkyne hydrogen atoms and H-bond acceptors. For example, JXNU-6a was found to exhibit large C_3H_4 uptake and efficient C_3H_4/C_3H_6 separation performance due to C—H···F hydrogen bonding interactions between the alkynyl

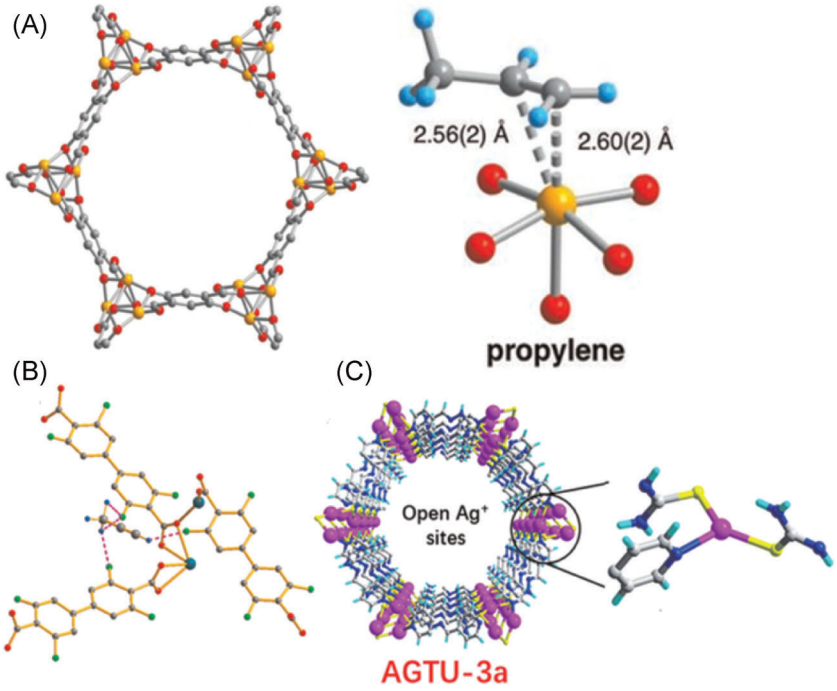


FIGURE 5 (A) Crystal structure of Fe_2(dobdc) (Left). The interactions between a propylene molecule and an unsaturated Fe site (Right). Orange, red, gray, and blue spheres represent Fe, O, C, and D atoms, respectively. (B) Hydrogen bonding interactions between C_3H_4 and fluorinated $TFBPDC^{2-}$ ligands in JXNU-6a. (C) The coordination sphere of open Ag+ atomic sites in AGTU-3a (reprinted with permission from Refs. 78,95,118. Copyright 2012, American Association for the Advancement of Science; Copyright 2020, American Chemical Society; Copyright 2019, The Royal Society of Chemistry)

hydrogen atoms of propyne molecules and the weakly basic fluorine atoms of fluorinated $TFBPDC^{2-}$ ligands (Figure 5B).[118]

π-Complexing agents: Strong π-complexes are typically formed between some transition metal ions (e.g., Ag^+, Cu^+, Pt^{2+}, and Pd^{2+}), and π-orbitals of unsaturated HCs.[144–147] Compared with sorbents containing common first-row transition metal (e.g., Cr, Mn, Fe, Co, Ni, Cu, and Zn), the former exhibit higher C_3H_6/C_3H_8 selectivity. AGTU-3a has open Ag^+ sites and displays a higher binding enthalpy and stronger interaction with propylene versus propane. This effect was attributed to Ag–π interactions (Figure 5C).[95]

4.1.2 | Van der Waals and supramolecular interactions

Van der Waals and supramolecular interactions can also play a role in selective recognition of C3 HC molecules as exemplified by $Co(AIP)(BPY)_{0.5}$ (5-aminoisophthalic acid [AIP]; 4,4′-bipyridine [BPY]) as reported by Qibin Xia's group.[109] As presented in Figure 6, C_3H_8 molecules are weakly bound in a single binding site by six weak C—H···π interactions between six hydrogen atoms of the C_3H_8 molecules and the BPY ligands. In addition, there are two C—H···O hydrogen bonds to O atoms of the AIP ligands. Conversely, C_3H_6 molecules interact with the framework via π···π interactions between C_3H_6 and two BPY ligands. This effect, coupled with smaller steric repulsion, allowed C_3H_6 to bind within a continuous region of the pore system while C_3H_8 was fixed to a single site, resulting in both a reduced uptake (0.48 mmol/g at 298 K) versus C_3H_6 (1.99 mmol/g at 298 K) and a lower diffusion rate (diffusion time constant of 0.0061 versus 0.1814 for C_3H_6 at 303 K), allowing for both kinetic and thermodynamic separation.

4.2 | Kinetic separation

Kinetic separation takes advantage of the variable diffusion rates of C3 HCs through pores to enable separation.[9] ZIF-8 is the first example of a PCN being evaluated for kinetic C3 separation as reported by Li et al.[88] As revealed by Figure 7, the kinetic separation of a propane and propylene gas is enabled by their different diffusion rates.

4.3 | Molecular sieving

Molecular sieving, also known as molecule size-shape sieving separation, or steric separation, is triggered by the pore aperture size of a particular PCN.[108] Y-abtc is an example of a molecular sieving material with optimal pore aperture size (4.72 Å) for C_3H_6/C_3H_8 separation.[93] This is because it adsorbs C_3H_6 (4.678 Å) with fast kinetics and blocks larger C_3H_8 molecules (4.3–5.118 Å) at room temperature and 100 kPa. However, most ultramicroporous materials that are suitable for sieving typically offer low selectivity and low uptake capacity because of the similar physicochemical properties of C3 HCs and the small pore volume of ultramicroporous PCNs.[89,148,149] Another limitation of sieving is that

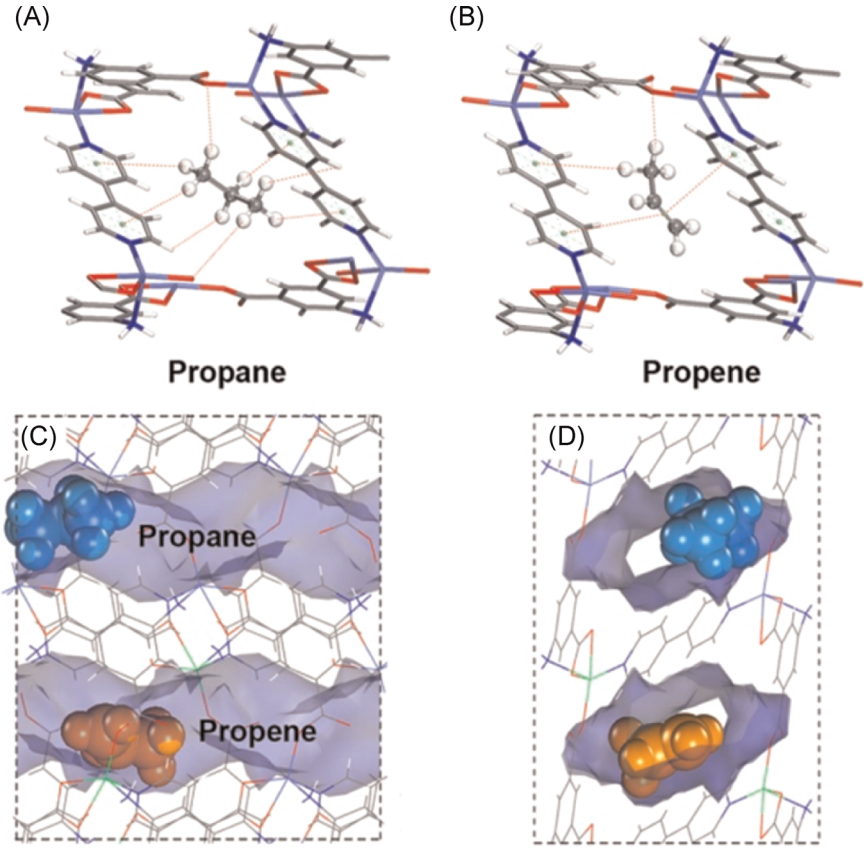


FIGURE 6 The preferred binding sites of $Co(AIP)(BPY)_{0.5}$ for C_3H_8 (A) and C_3H_6 (B). Schematic figure of C_3H_8 and C_3H_6 in the channel viewed, vertical (C) and along b axis (D). The violet shadow represents the inner channel wall (reprinted with permission from Ref. 109. Copyright 2019, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim)

selective adsorption of larger molecules from smaller molecules is infeasible and therefore C_3H_8/C_3H_6 separation is not a feasible goal by sieving.

4.4 | Gate-opening of flexible PCNs

The "gate-opening" effects that occur in many flexible PCNs typically result from structural transformations in response to stimuli such as light, pressure, heat, and guest molecules.[94,150,151] The differences in gate-opening pressure thresholds may depend on different types of gas molecules and the gas adsorption capacity may increase with these structural adjustments, allowing flexible PCNs to have excellent gas separation selectivity.[94,152–154] For example, MCF-57 exhibits guest-induced framework flexibility as reported by Tian et al.[110] This material showed strong C_3H_6/C_3H_8 separation performance due to very different responses to C_3H_6 and C_3H_8, in which C_3H_6 exhibited a significantly lower threshold pressure (Figure 8).

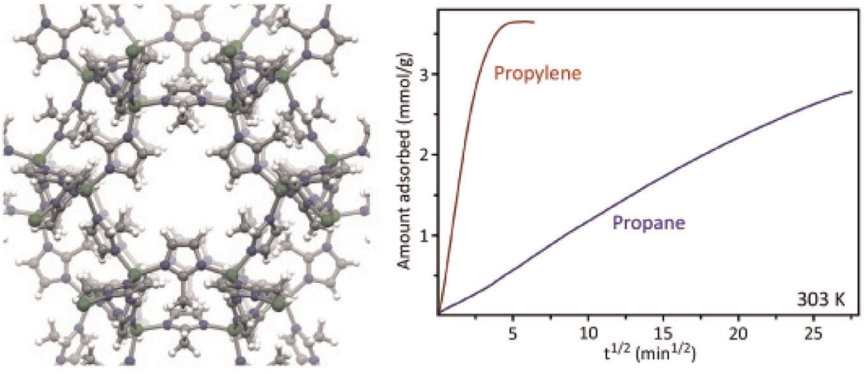


FIGURE 7 Kinetic separation of C_3H_6 from C_3H_8 by ZIF-8. (Left) Crystal structure of a portion of activated ZIF-8. Green, blue, gray, and white spheres represent Zn, N, C, and H atoms, respectively. (Right) Single component kinetic analysis of C_3H_6 and C_3H_8 uptake by ZIF-8 at 303 K and 0.8 bar (reprinted with permission from Ref. 88. Copyright 2009 American Chemical Society)

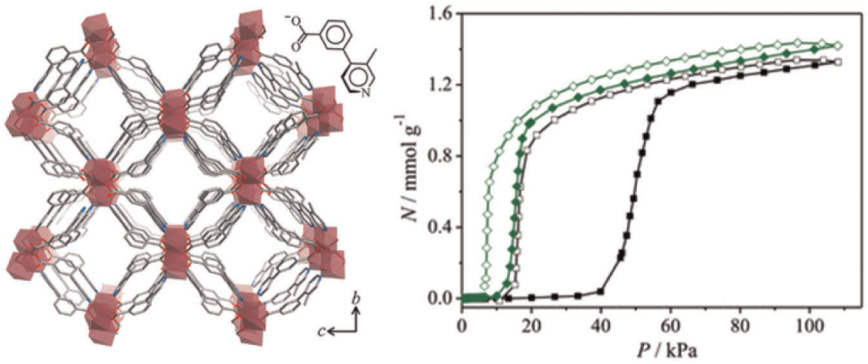


FIGURE 8 The coordination network MCF-57 (hydrogen atoms are omitted for clarity). (Right) C_3H_6 (green) and C_3H_8 (black) adsorption (solid) and desorption (open) isotherms of MCF-57 at 298 K (reprinted with permission from Ref. 110. Copyright 2020 American Chemical Society)

The investigated PCNs reveal excellent recyclability in most cases, and the flexible nature of the observed isotherms enhances their working capacities.[148] Gate-opening behavior endows flexible PCNs with a theoretically high separation performance compared to rigid analogs. However, in practice, separation experiments performed by breakthrough tests for gas mixtures are often inferior to predicted values from individual sorption isotherms owing to the possible coadsorption upon gate-opening which cannot be satisfactorily predicted by single-component isotherms.[96,120,143]

4.5 | Multiple mechanisms working together

In some sorbents, two or more of the four mechanisms discussed above may work synergistically to improve the efficiency of gas separation. For example, the dynamic ultramicropores (3.4 Å) of UTSA-200 allow for partial size-exclusion of larger propylene molecules, while the strong binding affinity of SiF_6^{2-} anions to alkynes over alkenes, when combined with framework flexibility, enables selective capture of propyne molecules.[71,155] The flexible CPL-1 material is another example of C_3H_6 separation from C_3H_8 enabled by synergy between gate opening and C−H···O hydrogen bonding.[92]

5 | CONCLUSIONS AND PERSPECTIVES

Separation and purification of C3 HCs play a vital role in the global chemical industry. In this review, we have detailed and analyzed recent progress with respect to the development of PCN sorbents for C3 HC separation and purification. These advances are enabled by the modularity of most PCNs, which allows for precise control over pore size, shape, and chemistry—a bottleneck for traditional classes of sorbents. Although there remains much to be addressed before industrial and commercial implementation of PCNs, the advances to date indicate great promise and provide the experimental and theoretical guidance to custom-design suitable adsorbents for optimal C3 HC separation. These challenges may also be seen as opportunities for the future growth of the field. In the following paragraphs, we discuss the further development of C3 HC separation by PCNs.

5.1 | Optimal pore size and chemistry

Most porous PCN materials are rigid 3D networks that exhibit Type I (Langmuir) adsorption isotherms. However, not all Type I isotherms are equally useful in this context. The most desirable isotherm type for separation occurs when the energetics of sorbent-sorbate interactions is in the range of 45–60 kJ/mol, that is, the energetic "sweet spot" for capturing a low concentration sorbate under ambient conditions. Much of the early interest in PCNs such as MOFs and PCPs were linked to their extra-large surface areas, which can be of utility, for example, in the context of gas storage and heterogeneous catalysis. However, large pores and cavities are unsuitable for strong sorbent-sorbate binding, except at very low loading if there is appropriate functionality. As loading increases, sorbate-sorbate interactions take over, meaning that there is no longer an energetic pull to enable binding at higher loadings. In essence, reduction in pore size is essential to optimize contact between adsorbates and adsorbents. Further, molecular sieving will be observed if pore apertures lie between the kinetic diameters of the sorbates of interest.[142,143] An approach that we have developed to address pore size and pore chemistry is to apply crystal engineering to study platforms (families) of closely related materials, thereby allowing fine control over the both pore chemistry and pore size while retaining pore shape. Perhaps the best example to date of this approach is the development of HUM platforms[156,157] for capture of trace CO_2[53,158] and C2 HCs.[50,155]

In general, C2 and C3 HC molecules share a number of common characteristics and in both cases design

principles for highly selective adsorbents are based on tailoring of pore size and pore chemistry. It has become evident that the leading sorbents for the separation of most C2 and C3 gas pairs are ultramicroporous and have sorbent-sorbate-specific binding sites, leading to highly selective uptake.[100] However, it is noteworthy that the C3 sorbates have larger kinetic diameters than their C2 counterparts. Further, whereas three of the four C3 adsorbate molecules have permanent electrostatic dipoles, none of the C2 molecules do. This suggests a need for greater specificity in molecular recognition for the design of selective binding sites for C3 adsorbates as all four C3 molecules may selectively bind to a sufficiently heterogeneous adsorbent surface. As more systematic studies of high-performing C3 adsorbents become available, the design strategies that can offer specific C3 binding sites will become increasingly clear.

5.2 | Lack of understanding and/or control over kinetics and coadsorption

Slow kinetics or coadsorption may render materials with promising equilibrium behavior unsuitable for real applications. Whether or not a given porous material will exhibit suitably fast kinetics and/or coadsorption in industrially relevant conditions remains poorly understood. Intuitively, one would expect that narrow pores result in slower kinetics, but this is not necessarily the case as we have shown for CO_2 sorption.[53] Ideally, a sorbent should load and unload within minutes in pressure, temperature, or vacuum swing separation processes. Theoretically, it is impossible to totally eliminate coadsorption phenomena during the gas adsorption process, especially when the separation is not based on molecular sieving, that is, all the gas molecules can permeate the pore. For molecular sieving separations, coadsorption can be suppressed to realize high purity C3 HC purification. Unfortunately, there is likely to be a trade-off between working capacity and selectivity in ultramicroporous materials as discussed below.

5.3 | The trade-off between adsorption capacity and selectivity

Typically, high uptake of a gas arises due to the high porosity of the host framework; however, high porosity commonly leads to low selectivity for the reasons outlined earlier. More judicious selection of pore size may enable increased selectivity in the gas separation in PCNs, but uptake capacity might be killed, as exemplified in the case of molecular-sieving of propylene over propane.[89] A low density of immobilized binding sites on a large pore surface can lead to high gravimetric gas uptake but poor selectivity other than at low loading. To overcome this trade-off between adsorption capacity and selectivity, various strategies have been explored. The "dual-functionality" approach, whereby an optimal pore aperture and specific binding sites are systematically integrated to balance highly selective separation performance and high uptake capacities, is such an example.[50] From a structural perspective, PCNs possessing large cages functionalized by a high density of specific binding sites interconnected through one-dimensional channels with small apertures is a promising approach. Recently, a "core-shell" approach also promises to address the trade-off between uptake and selectivity as exemplified by the hybrid bio-MOF-11/14.[159] In this particular sorbent, a smaller-pore shell grown onto a highly porous isoreticular core enabled high selectivity and limited loss of uptake.

5.4 | Inverse adsorption of propane over propylene

Typically, PCN adsorbents have a higher affinity for propylene than propane thanks to its smaller size, larger dipole moment, and stronger sorbate-sorbent interactions arising from the π-electrons of the propylene double bond. As a result, PCNs tend to retain propylene whereas propane breaks through first in binary gas separations. Whereas adsorbed propylene can be collected by column regeneration, coadsorption can hinder the harvesting of high-purity propylene streams unless molecular sieving-based adsorbates are used. Furthermore, the production of highly pure propylene by desorption is still a moderately energy-intensive process. In contrast, propane-selective columns can remove trace propane from a gas stream to afford polymer-grade propylene in a single and relatively simple separation step. Therefore, it is desirable to develop propane-selective PCNs for efficient adsorptive propylene/propane separations. The key unmet need is a sorbent that preferentially removes propane from propylene with sufficiently high selectivity for trace removal. Further, in the absence of lead or "generation 1" sorbents, the factors that influence selective adsorption of propane over propylene in PCNs are not well understood and lack systematic investigation. Recent reports that address inverse separation of ethane over ethylene by PCNs[160–162] suggest that it is only a matter of time before sorbents that offer highly selective inverse C3 HC separation become available.

5.5 | One-step purification of propylene from multicomponent C3 HC mixtures

For the purposes of acquiring polymer-grade propylene, it is necessary that all impurities except propylene are preferentially removed by adsorption from a mixed gas feedstock, thus directly generating pure propylene downstream of the separation beds or columns. However, this is highly challenging to achieve using PCNs due to the lack of effective propane-selective adsorbents and the difficulty in fully removing other impurity gases and vapors such as CO_2, SO_2, and water, in addition to propyne and propadiene, that are present in industrial gas streams. One might envisage that a single PCN could simultaneously remove multiple trace impurities, but no single sorbent has yet demonstrated such performance.

Recently, our group developed an alternate approach, synergistic sorbent (SYNSORB) separation, to address the need for removal of multiple impurities in the context of one-step production of polymer-grade C_2H_4 from ternary ($C_2H_2/C_2H_6/C_2H_4$) or quaternary ($CO_2/C_2H_2/C_2H_6/C_2H_4$) gas mixtures. The approach used was to arrange a series of custom physisorbents in a packed-bed.[156] Figure 9 illustrates how SYNSORB can enable one-step purification of a four-component gas mixture that contains trace impurities through the use of be spoke sorbents tasked for each of the trace impurities. Polymer-grade C_2H_4 (>99.9%) was obtained even for the challenging and industrially relevant 1:33:33:33 mixture of $C_2H_2/C_2H_4/C_2H_6/CO_2$. This method is not limited to C2 compounds, but could also be suitable for C3 HC separation. The key unmet need is a sorbent to that has high enough selectivity to remove propane from propylene, as mentioned above.[112–115] Such a material would enable a SYNSORB approach to produce propylene from multicomponent C3 HC mixtures of propane, propyne, and propadiene in one-step. SYNSORB, therefore, lays the groundwork to enable new one-step technologies for addressing the energy footprint of high-volume C3 HC gas separations.

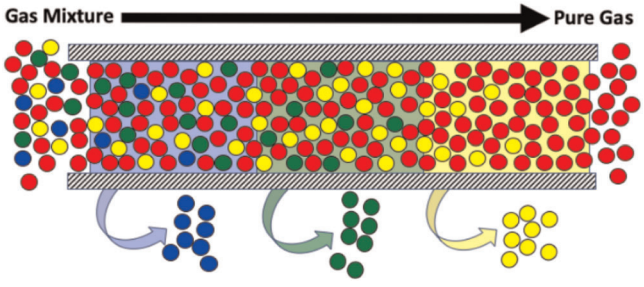


FIGURE 9 The SYNSORB concept: three bespoke sorbents are each tasked to remove one impurity of a four-component gas mixture (reprinted with permission from Ref. 156. Copyright 2019, American Association for the Advancement of Science)

5.6 | Flexible PCNs for separation

Flexible PCNs have garnered increasing attention as sorbents for gas separation because of their reversible and sorbate-induced phase transformations, which can yield large operational working capacities and favorable energetics. However, there are unknowns regarding separation mechanisms such as the impact of coadsorption after gate-opening and resultant reduced selectivity. Consequently, single-component isotherms may be poor predictors of separation performance. Rather, adsorption experiments using mixed gases or breakthrough experiments are needed to determine efficacy. Recently, a subclass of flexible PCNs that exhibit switching between nonporous phase and porous phases induced by gases has attracted attention.[30,134–138] Usually, differences in affinity for sorbates, or the molecular recognition of the host for a given sorbate, result in distinct gate-opening threshold pressures, thus facilitating the separation of gases using a "soft" material. An ideal scenario would be for propyne to trigger the switching of a flexible PCN at ambient temperature and low pressure, while propylene does not under the same conditions. This could allow for separation even with an unbalanced ratio between the two gases provided coadsorption of the larger propylene is minimal. The separation of C3 HCs by flexible PCNs is an appealing concept but more studies are required to address separation performance of the open phase and elucidate the underlying mechanisms that drive gate-opening.

5.7 | Stability and recyclability of PCNs

Poor mechanical stability, low thermal stability, and poor hydrolytic stability are common pitfalls that can limit the commercial viability of PCNs. To retain performance in real world operating conditions, sorbents must possess good thermal and chemical stability, including hydrolytic stability and high tolerance to reactive impurities. Water vapor is ubiquitous, reactive with many coordination sites, and exhibits a small kinetic diameter. There is therefore a high risk of nucleophilic attack of labile metal centers in PCNs and associated loss of porosity. Although related work has detailed that PCNs based upon high valence metals can dramatically improve water stability, their utility for separation performance for C3 HCs remains under studied.[163] It remains a challenge to find water, acid, or base-stable PCNs that fulfill the stability criteria for practical C3 HC separation.

Recent reports have demonstrated that interpenetration or catenation can improve the stability of PCNs and fine-tune pore size, allowing for a compelling approach to the

design and fabrication of sorbents with benchmark separation performance for several challenging gas mixtures. Other strategies include modification of the parent sorbent with hydrophobic groups via predesigned ligands,[164,165] by postsynthetic modification[166] or through formation of composites with hydrophobic polymers[167,168] to afford water-resistant PCNs.[169] An additional concern involves the regeneration of strong adsorption sites such as UMCs, which can lead to high energy footprints that limit the energy efficiency of the solid-state sorption approach.

5.8 | Separation performance under humid conditions

H_2O (along with H_2S) is present in natural gas streams and may find its way downstream in C2 and C3 mixtures due to its small molecular size and ubiquity. H_2O is known to have a detrimental impact on sorbent performance and is typically removed from HC streams by the use of solvents or molecular sieves.[5] Therefore, the design of sorbents whose performance is unaffected by the presence of H_2O is an important goal that may assist in lowering the energy footprint of purification processes even further.[160,170,171]

Compared with C3 HCs, water molecules are prone to preferentially interact with hydrophilic recognition sites located on the pore surface, especially UMCs and hydrogen bonding acceptors/donors. Such binding is usually detrimental to separation performance in terms of both uptake and selectivity. The design of hydrophobic PCNs via direct synthesis or postsynthetic modification could prove effective in achieving greater selectivity for C3 HCs over water vapor.

5.9 | Scalability, cost, and manufacturing

Most existing PCNs are prepared by solvothermal synthesis or rely upon custom-made linker ligands, many of which require involved organic synthesis. These factors hinder commercial viability for anything but low volume niche applications. Before the commercial usage of PCNs as sorbents for C3 HC separation, capital costs should be carefully evaluated and considered based on large-scale synthesis methodologies. Continuous and solvent-free synthetic methods have been applied to produce PCNs where the availability of organic ligands would be the only concern.[172] Nevertheless, the cost of raw materials (metals and linkers) is one parameter that can be easily controlled by the researcher. Another consideration is the shaping or pelleting of MOFs, which is necessary because of engineering considerations. Pelletization is likely to lead to adsorption capacity loss and requires high mechanical stability. Accordingly, the adsorption characteristics of MOF pellets should be comprehensively investigated from a thermodynamic and kinetic point of view, while also keeping in mind process and manufacturing considerations. It is worth mentioning that there are indications that PCNs can lose their adsorption or separation performance once they are formulated into compacted particles or pellets.[173,174] Mechanical instability due to the stresses of formulation and recycling are crucial, yet under-explored, risks.

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